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Halon Options Technical Working
Conference, Albuquerque, NM,
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Building and Fire Research Laboratory*

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U.S. Department of Commerce
Donald L. Evans, Secretary

Technology Administration
Phillip J. Bond, Under Secretary for Technology

National Institute of Standards and Technology
Arden L. Bement, Jr., Director

EVALUATION OF TRANSITION METALS FOR PRACTICAL FIRE SUPPRESSION SYSTEMS

D. McDonnell, B. Z. Dlugogorski and E. M Kennedy
Process Safety and Environment Protection Research Group
Faculty of Engineering and Built Environment
The University of Newcastle
Callaghan, NSW 2308

Phone: +61 2 4921-6176; Fax: +61 2 4921-6920
Email: cgbzd@alinga.newcastle.edu.au

ABSTRACT

Extinguishment of low strain-rate diffusion flames with fine water mist was investigated in an opposed-flow burner. The mist, characterised by the volume-average diameter of its particles of $8.6\ \mu\text{m}$, was generated by atomizing 0.86 M solutions of chloride salts of cobalt and nickel. The mist was introduced into the air stream at the nominal strain rate of between 20 and $40\ \text{s}^{-1}$. CoCl_2 and NiCl_2 demonstrated similar inhibitory properties, significantly exceeding the effectiveness of pure water mist. Both salts were found to increase the heat extraction capacity of pure water mist by 1%. Thus the enhancement of flame inhibition by solutions of CoCl_2 and NiCl_2 indicates chemical activity of cobalt and nickel in the flame. The study concludes that solutions of salts of the two transition metals display similar effectiveness to the solution of NaCl and are therefore economically unviable for practical fire suppression systems.

INTRODUCTION

The transition metals such as chromium, iron, lead, manganese or tin have been found to be extremely potent fire suppressants, when delivered at low concentrations to flames. Once the metal concentration exceeds 100 ppm for iron (Rumminger et al., 1998), 200 ppm for manganese and 2000 ppm for tin (Linteris, 2001a) little extra effectiveness is gained by the addition of more metals. This occurs because of precipitation of metal compounds from the gas phase due to their low vapour pressure (Rumminger and Linteris, 2000). Attempts to redress this situation by adding a mix of metals to flames have failed to raise significantly the suppression effectiveness (Linteris, 2001b). Thus, it is unlikely that practical transition metal-based fire suppressants can be developed which rely only on the chemical interaction of these metals with flames.

One possibility is to deliver particles of carbonate salts of transition metals to flame to take advantage of the endothermic decomposition reactions, similar to alkali metal salts in the so-called dry chemicals (eg. Ewing et al., 1992). Another possibility is to combine transition metal salts together with different suppression agents. These could be inert gases, such as N_2 or CO_2 , weakly chemically-active gases such as HFCs and active chemical agents such as CF_3I ¹ or phosphorous containing compounds. One may also use water mist generated from solutions of transition-metal salts to take the advantage of the physical and chemical suppression mechanisms offered by such extinguishants, as done for cup-burner flames by Shilling et al. (1998) for Mn and Linteris (2001b) for Fe, Mn and Sn.

The aim of the present investigation was to examine the suppression effectiveness of transition metals in laboratory experiments under conditions that are similar, as much as possible, to those of practical applications. For this reason, we have selected low strain-rate diffusion flames which exist in real fires, and have used water mist generated from solution of salts of transition metals to ensure global extinction. Transition metals are known to perform significantly better in premixed than diffusion flames (Linteris 2001b), though the latter are more typical of real fires. In this study, we have also compared the fire-suppression performance of solutions of transition-metal salts with that of NaCl solution to determine whether they offer significant advantages over alkali metals, and whether their use is justified in water-mist systems.

EXPERIMENTAL

Figure 1 shows a schematic of the counter-flow burner producing an axis-symmetric laminar diffusion flame. If the flame is located on the oxidant side of the stagnation plane (as is the case with methane/air flames), the strain rate is defined as the maximum velocity gradient on the oxidant side of the flame. The local strain rate in flame may be measured experimentally using laser-Doppler velocimetry. Alternatively, it is possible to calculate the global strain rate from the following expression (MacDonald et al., 1999):

¹ Production of $CBrF_3$ has ceased in industrial nations, so this agent cannot be considered as a viable option in practical fire-suppression systems.

$$a = \frac{2v_o}{L} \left(1 + \frac{v_F \sqrt{M_F}}{v_o \sqrt{M_o}} \right). \quad (1)$$

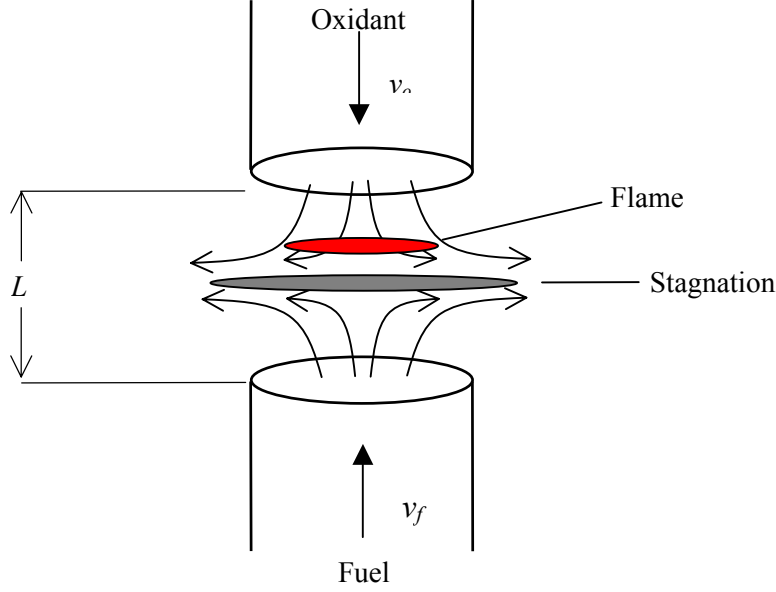


Figure 1. Schematic of axis-symmetric strained laminar counter flow diffusion flame.

In Equation 1, v is the velocity of the incoming stream, L is the separation distance of the two burner nozzles, M is the molecular weight and the subscripts O and F refer to oxidant and fuel streams respectively.

Detailed description of the experimental apparatus has been recently published elsewhere (McDonnell et al., 2000a). Here, we provide an overview of its most important features of the apparatus. As shown in Figure 2, two mass controllers gauge natural gas and air flows, with the air stream passing through the atomiser to entrain mist droplets. The diameters of the oxidant and fuel burners are 5 and 1 cm, respectively. Since the air burner is much larger than fuel burner, no nitrogen shroud gas is used. The air burner is cooled with water to avoid premature evaporation of the mist. The mist produced has 50% of the volume of its droplets below $8.2 \mu\text{m}$ (Shilling et al., 1996). The burner design is similar to that used by Kent and Williams (1975).

Table 1 lists strain rates investigated, and the relevant conditions at each strain rate, where S is the distance of the stagnation plane from the oxidiser nozzle. The burner geometry utilised restricted the study to low strain rates ($<120 \text{ s}^{-1}$). In addition, the introduction of mist into the flame by air-inducement further limited the strain rates to below 40 s^{-1} . Higher strain rates could only be obtained by large air flow rates, which diluted the mist loading (g/m^3 air) obtained at the maximum humidifier setting to a level insufficient to extinguish the flame.

Note that the stagnation plane is located where the momenta of the opposing flows are balanced. Assuming that the incoming streams are at the same temperature and pressure conditions, S can be obtained from the following expression:

$$S = \frac{L}{\left(1 + \frac{v_F \sqrt{M_F}}{v_O \sqrt{M_O}}\right)}. \quad (2)$$

Table 1. Summary of the conditions studied; the separation of the two nozzles (L) is 9 mm.

Strain rate, a (s ⁻¹)	Oxidant velocity, v_F (m/s)	Fuel velocity, v_O (m/s)	S (mm)
40	0.0819	0.1188	5.94
	0.0977	0.1073	5.36
35	0.0714	0.1042	5.96
	0.0819	0.0965	5.51
30	0.0608	0.0895	5.97
	0.0714	0.0818	5.45
25	0.0503	0.0749	6.00
	0.0608	0.0672	5.37
20	0.0397	0.0603	6.00
	0.0503	0.0526	5.25

The metal salt was first dissolved into a solution of distilled water, producing a solution of predetermined concentration, to be placed into the mist production system. It was necessary to clean the make-up, metering and humidifier reservoirs with distilled water, and then dry each reservoir as thoroughly as possible. The salt solution was then placed into all the reservoirs, and the system was allowed to operate for a few minutes to reach steady state.

To determine the extinction induced by each metal salt, the following procedure was implemented: A stable flame was established at a constant strain rate, and the rate of mist production was increased to the point of global extinction. The flame was then re-established at a higher strain rate and the procedure repeated. The overall procedure was repeated for each metal salt solution studied. These consisted of 0.86 M solutions of CoCl₂, NiCl₂, FeCl₂ and NaCl. The results from CoCl₂ and NiCl₂ experiments were compared with the data from NaCl runs, reported previously (McDonnell et al., 2000a). The iron chloride solution attacked the hinge of the float valve with rust, preventing the smooth working of the valve. This resulted in a staccato cycle wherein the humidifier level drained low before being replenished. For this reason, the FeCl₂ data were judged unreliable and are not included in this article.

RESULTS AND DISCUSSION

Glassman (1996) proposed a simple model for determining whether a metal would combust in the vapour phase, or undergo heterogeneous surface burning. Glassman's criterion for the vapour-phase combustion of metal states that for a metal to burn as a vapour, the temperature of the oxide boiling point must be greater than the temperature of the metal boiling point (Glassman, 1996). If this criterion is extended to the present case of CoCl_2 and NiCl_2 , the Glassman model would predict the gas phase oxidation of Co and Ni, provided that the boiling point temperature of metal oxides are higher than those of CoCl_2 and NiCl_2 . However, the Glassman criterion could not be directly applied to Co and Ni, as the boiling point temperatures of these oxides were not known. As a first approximation, the boiling point temperatures may reasonably be assumed to be larger than the melting point temperatures, on the assumption that the substance does not sublime. Table 2 shows the relevant boiling and melting point temperatures, together with the heat of vaporisation (ΔH_v) and the heat of the global oxidation reaction (ΔH_o) CoCl_2 and NiCl_2 .

Thus the Glassman criterion predicts homogenous oxidation of CoCl_2 and NiCl_2 . The relatively high melting point temperatures of the oxides may indicate that significant fractions of CoO and NiO exist as heterogenous agents in the flame.

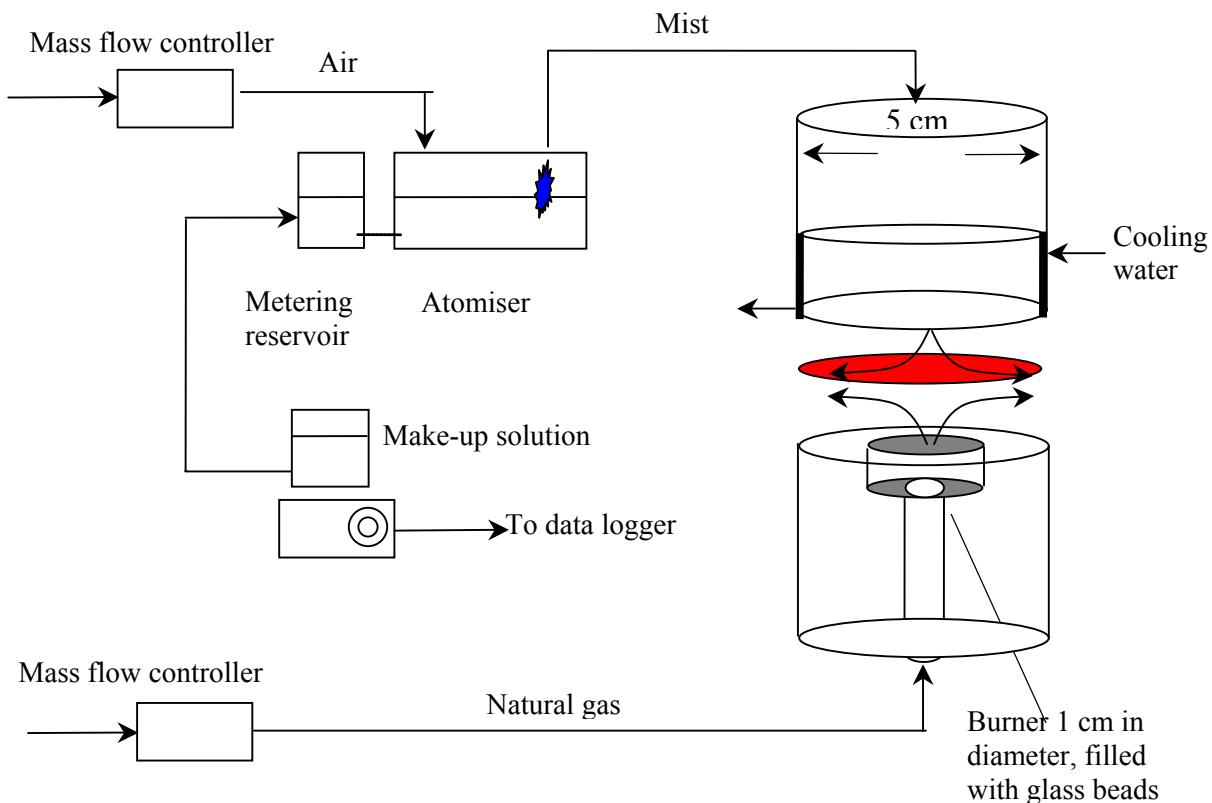


Figure 2. Schematic of the experimental apparatus.

The flames doped with transition-metal mist burned with a whitish glow, with a marked streaked appearance. This phenomenon has been previously noted (Shilling et al., 1996), and a possible explanation was advanced by Bulewicz & Padley (1975) that the streaks indicated the presence of an involatile oxide. In the present study, the streaks were particularly noticeable in additional experiments performed with solution of FeCl₂. This observation agrees well with the very high boiling point temperature of iron oxide (3687 K) and with the conclusion reached by Rumminger and Linteris (2000) about the deteriorating effectiveness of Fe at higher concentration of iron, as a consequence of the very low vapour pressure of Fe compounds.

Table 2. Boiling and melting point temperatures. ΔH_v was calculated as the residual of the heat of fusion subtracted from the heat of sublimation (Aylward & Findlay, 1994). ΔH_o was calculated using Hess' law of heat summation. The heat of sublimation of NiO was known (554 kJ/mol), but not the heat of fusion. Heat of vaporisation can therefore be estimated to be 500 ± 50 kJ/mol.

	T boiling (K)	T melting (K)	ΔH_v (kJ/mol)	ΔH_o (kJ/mol)
CoCl ₂	1322		199	75
NiCl ₂	1246, sublimes		170	65
CoO		2068		
NiO		2257	~500	

Figure 3 shows the extinction data obtained for CoCl₂ and NiCl₂, expressed in g of mist of pure water or salt solution per m³ of air. The data presented in Figure 3 are of a much greater uncertainty than that obtained for the alkali (McDonnell et al., 2000a) and alkali earth metals (McDonnell et al., 2000b) and only points of some reasonable certainty are presented. In particular, solutions of CoCl₂ interfered with the apparatus, often preventing meaningful readings from being obtained. Cobalt chloride was prone to crystallise out of solution during the experimental investigation. After time, this blocked the small inlet to the metering reservoir, and prevented the replenishment of the humidifier, interfering with the measurement of the rate of mist production.

Figure 3 demonstrates that the inhibition effects of cobalt and nickel to be quite similar, with cobalt perhaps slightly more effective on both a molar and mass basis. Note that the critical loading of pure water mist at extinguishment agrees well with the results obtained by Shilling et al. (1998) from cup-burner experiments. The physical effects associated with crystallising and evaporating NiCl₂ and CoCl₂ contributed less than 1% to the heat extraction processes relative to the water mist. Therefore, the enhancement of flame inhibition observed here indicates chemical activity of the transition metals in the flame.

Figure 4 compares the inhibition effect provided by the transition metals in comparison to that provided by sodium. The figure shows no clear advantage of replacing NaCl with NiCl₂ and CoCl₂ in practical applications.

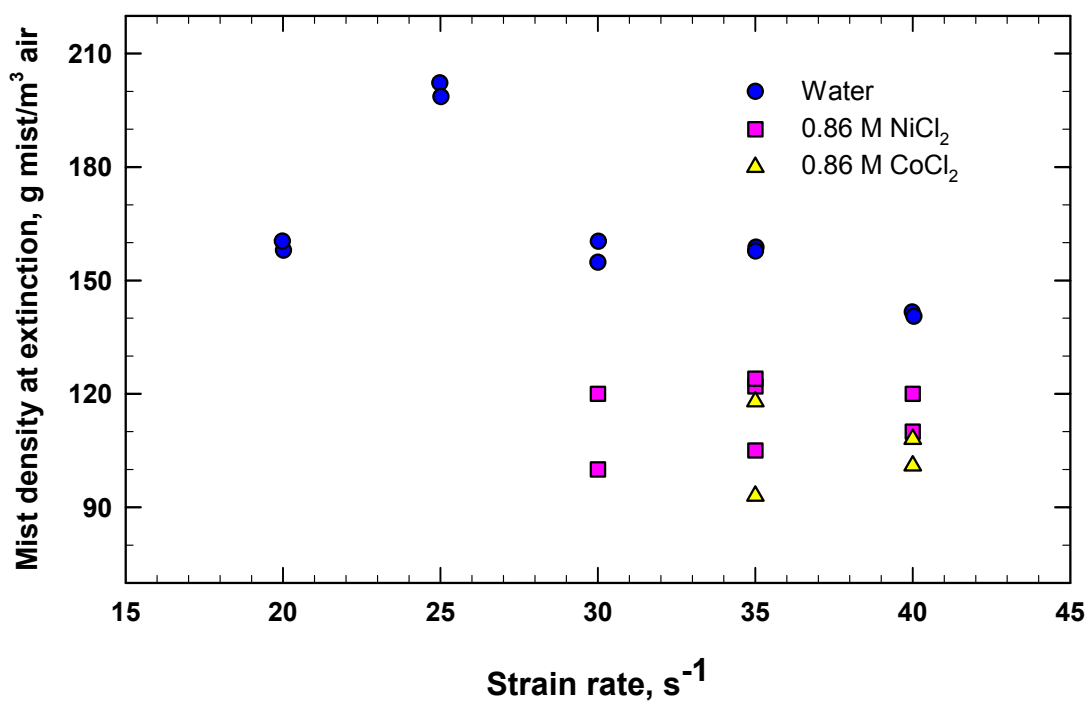


Figure 3. Comparison of the inhibition effects of water mist with solutions of NiCl_2 and CoCl_2 .

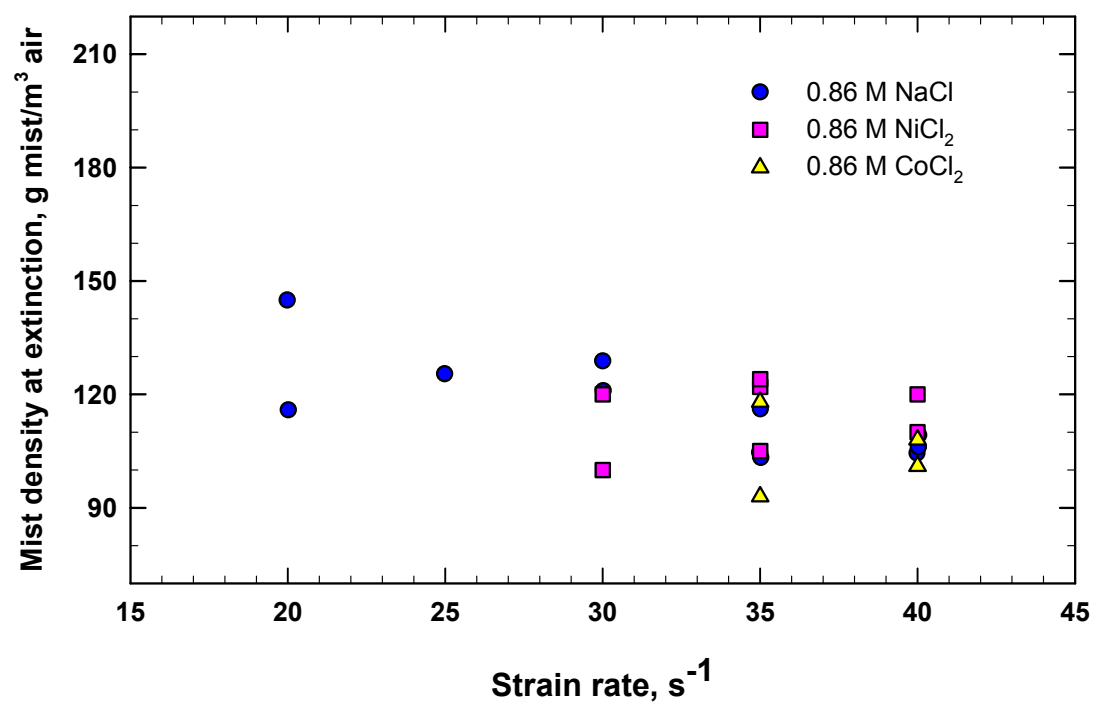


Figure 4. Comparison of the inhibition effects of NaCl with solutions of NiCl_2 and CoCl_2 .

For the unenclosed flames considered in this study, the effect of oxygen dilution (or the so-called enclosure effect) is small in comparison to the effect of thermal capacity of water vapour and the latent heat of water (Dlugogorski et al., 1998). This situation is very different from that which occurs in enclosed fires. Such fires can be extinguished by water mist at concentration of about 40 g/m^3 , due to the effect of enclosure (Vaari, 2002). From this standpoint, one can raise a valid objection about the utility of the present data. The results reported in this paper apply only to suppression of open-space fires, which necessitate the delivery of 180 g of mist per m^3 to the flames. In practice this is often difficult to achieve and depends critically on design details of a given system. For solution of metal salts, the required amount is only 130 g/m^3 . The difference could be significant for extinguishment of marginal fires for which the design pure-water concentration is not reached.

CONCLUSIONS

It has been found that both cobalt and nickel exhibit strong chemical activity to mitigate flames. It is proposed that the full potential of these metals as flame suppressants cannot be fully realised due to condensation of their oxides. The overall performance of solutions of NiCl_2 and CoCl_2 is comparable to that of NaCl . Thus there is no practical advantage of using either of these transition metals for fire suppression.

ACKNOWLEDGMENTS

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